



Environmental Effects of Dredging Technical Notes



FACTORS INFLUENCING BIOACCUMULATION OF SEDIMENT-ASSOCIATED CONTAMINANTS BY AQUATIC ORGANISMS; FACTORS RELATED TO CONTAMINANTS

PURPOSE: This is the first technical note in a series of four which outlines and describes the principal factors that determine uptake and retention of chemicals by aquatic organisms. The first three notes describe factors related to contaminants, sediment and water, and biota. The fourth note is a glossary and bibliography. The information contained herein is intended to assist Corps of Engineers environmental personnel in activities requiring a working knowledge of concepts and terminology in the subject of chemical uptake, retention, and elimination by aquatic organisms exposed to contaminated sediments.

BACKGROUND: Bioaccumulation is the general term used to refer to the uptake and storage of chemicals by organisms from their environment through all routes of entry. Bioaccumulation includes bioconcentration, which is the direct uptake of chemicals from water alone, and is distinguished from biomagnification, which is the increase in chemical residues taken up through two or more levels of a food chain. Assessments of the potential for bioaccumulation of toxic substances associated with dredged sediments are often required in evaluations of permit requests. Thus, familiarity with the fundamental physical, biological, and chemical factors affecting bioaccumulation is necessary for performing evaluations of the ecological impacts of dredging operations. Additionally, a basic understanding of the concepts and terminology of bioaccumulation is increasingly required of environmental personnel who are involved in dredging and disposal operations which may involve contaminated sediments and legal personnel involved with regulation and litigation.

These notes are intended to serve as a source of basic information and to provide a guide to the scientific literature for each topic discussed. The emphasis is on factors affecting bioaccumulation of sediment-associated chemicals. A brief discussion of each factor is given and a list of references is provided. The references are extensive and frequently bear on more than one topic. An effort has been made to select both historically important works and the most recent research reports in each area. Numbers in parentheses following the subject headings locate the references for each subject. Papers referenced are alphabetized for each subject for easy identification of those most pertinent to the reader's interest. The glossary of technical terminology is presented in the fourth note in the series.

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The subjects discussed in these notes reflect current research for which new findings constantly appear in the literature. Consequently, the discussions and interpretations are based on inference and best judgement regarding the interactions of factors influencing bioaccumulation and represent the best understandings of the authors. Readers are encouraged to consult the literature cited.

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Fugacity (1-12)

If a chemical is introduced into a closed system consisting of two immiscible phases, e.g., an oil and water, it will distribute itself between the two phases until equilibrium is reached. At equilibrium there will continue to be an escape of individual molecules from the oil to the water, and vice versa, but the net exchange of chemical mass between the two phases will be equal to zero. This tendency of a chemical to escape from a phase is referred to as its "fugacity" (from the Latin fuga for "flight"). Fugacity is a corollary function of chemical potential and just as, by definition, equilibrium exists when the chemical potential in all phases of a closed system is equal, equilibrium also exists when the fugacities of a chemical in the phases are equal.

At the low concentrations typical of environmental contamination, fugacity and concentration can be directly related by a constant that quantifies the ability of a phase to contain the chemical. An example of this "containing ability" is the mass of a chemical that could be solubilized in a given volume of water under standard conditions. A different mass of the same chemical could be solubilized in an equal volume of an organic solvent, such as oil. That is, the containing ability of the oil would be more or less than the containing ability of the same volume of water for the chemical.

Partition coefficients express the concentration differential between two phases at equilibrium. This is the essence of the concept of "equilibrium partitioning" and is fundamental to understanding the processes of chemical bioavailability and bioaccumulation. Fugacity and equilibrium partitioning are thermodynamic concepts, i.e., they are independent of rates of change (kinetics) or of rate-influencing processes. Rate-influencing processes determine how long

it takes to reach an equilibrium between chemical concentration in a source phase and in a sink phase, but not how much chemical will be in each when the equilibrium is reached. "Bioaccumulation potential," as the term is used throughout these notes, is intended in the thermodynamic sense. The bioaccumulation potential of a chemical is dependent on the fugacity of chemicals and the containing abilities of sediment and organism as the phases of concern. The actual quantity of chemical that may be bioaccumulated is influenced by a multitude of variables. The discussions that follow consider many of these rate-influencing variables as well as variables affecting bioaccumulation potential.

Hydrophobicity (13-18)

Literally, "fear of water," hydrophobicity is the property of neutral (uncharged or nonpolar) organic molecules that causes them to associate with surfaces or with organic solvents rather than to remain in aqueous solution. The presence of a neutral molecule causes the highly charged molecules of water in its vicinity to link up in what has been described as a "shaky cage" structure around the neutral molecule. This structuring of water is energetically unfavorable and the neutral molecule tends to seek a less energetic phase if one is available. Animal lipids, mineral surfaces, or associations of other neutral molecules are examples of phases that are less energetic than water. In an operational sense, hydrophobicity is the reverse of aqueous solubility.

The octanol/water partition coefficient of a chemical (K_{ow} , $\log K_{ow}$, or $\log P$) is a measure of its hydrophobicity. K_{ow} is a constant that describes the magnitude of the difference between the solubility of a chemical in water and its solubility in the organic solvent, octanol. Octanol serves as a good surrogate for animal lipids in the laboratory as organic chemicals are soluble in both to about the same extent. Because organic chemicals accumulate in the lipids of organisms, hydrophobicity measurements provide good indications of the tendency for organic chemicals to bioconcentrate and bioaccumulate. Bioconcentration factors (BCF) increase with increasing hydrophobicity up to a $\log K_{ow} \approx 6.00$. At hydrophobicities greater than $\log K_{ow} \approx 6.00$, BCFs tend to decrease.

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Solubility (13, 19-24)

In general, as the water solubility of chemicals increases, bioaccumulation decreases. Water solubility favors rapid uptake of chemicals by organisms but at the same time favors rapid elimination. Any physical or chemical process that increases the water solubility of a chemical decreases the tendency for that chemical to bioaccumulate. Organic chemicals that form weak acids or bases and those that can be protonated (e.g., sulfonate and tertammonium surfactants) bioaccumulate to lower concentrations than do neutral organics not only because they are more reactive, but also because these processes make them soluble. Compounds such as chlorinated phenols are sometimes referred to as "hydrophobic acids" because the chlorinated benzene nucleus favors partitioning to lipid and other organic phases, while the phenolic oxygen confers aqueous solubility. Such compounds are also reactive and do not usually bioaccumulate to high levels. Organic compounds that do not dissociate (neutral or nonpolar organics) are increasingly insoluble as molecular mass increases and are the most highly bioaccumulating. Although the ionized forms of heavy metals such as mercury, cadmium, and lead are soluble in water, these substances bind with tissues and thus are actively bioaccumulated by organisms.

Stability (25-30)

For chemicals to bioaccumulate, they must be stable, conservative, and resistant to degradation. Metals are inherently conservative since they are elemental in nature. Metals are taken up by organisms either as ions in solution or as organometallic complexes. Complexation of metals may facilitate bioaccumulation by increasing bioavailability. Organometalloids that are taken up by organisms may hydrolyze, allowing the free metal ion to bond ionically or covalently with sulfhydryl, amino, purine, and other reactive groups present in endogenous substrates.

Organic compounds with structures that protect them from the action of enzymes or from nonenzymatic hydrolysis tend to bioaccumulate. However, chemicals such as the phosphate ester pesticides (e.g., parathion and malathion) do not bioaccumulate because they are easily hydrolyzed and the products eliminated. Polynuclear aromatic hydrocarbons (PAHs) are also easily broken down and

eliminated by most fishes and many other organisms, although some invertebrates, such as bivalve mollusks and amphipods, have low metabolizing capability for these compounds. The presence of electron-withdrawing substituents on PAHs tends to stabilize these compounds. Chlorines, for example, are bulky, highly electronegative atoms that tend to protect the nucleus of an organic molecule, such as a PAH, against chemical attack. Highly chlorinated organic compounds such as the polychlorinated biphenyls (PCBs) bioaccumulate to high levels because they are easily taken up by organisms and cannot be readily broken down and eliminated.

Stereochemistry (14, 31-42)

The spatial configuration or shape, i.e., stereochemistry, of a neutral molecule affects its tendency to bioaccumulate. Molecules that are planar, such as PAHs, dioxins, or certain of the PCBs, tend to be more lipid soluble than globular molecules of similar molecular weight. For neutral organic molecules, planarity generally correlates with higher bioaccumulation unless the molecule is easily metabolized by an organism, as is the case, for example, with PAHs in most fishes.

Hydrophobicity and transport across biological membranes are affected by the size as well as shape of molecules. Hydrophobicity of neutral molecules generally increases with molecular mass, volume, or surface area. Neutral molecules that have cross-sectional dimensions greater than about 9.5 Å have been described as "sterically hindered" in their ability to penetrate the polar surfaces of the cell membranes in fish gut or gill tissue. The limited bioaccumulation of compounds such as octachlorodibenzo-p-dioxin (9.8 Å) or decabromobiphenyl (9.6 Å) has been attributed to steric hindrance. Many of the properties of molecules that play a role in bioaccumulation (e.g., hydrophobicity, solubility, vapor pressure, and dissociation constant) may be predictable from their molecular structures.